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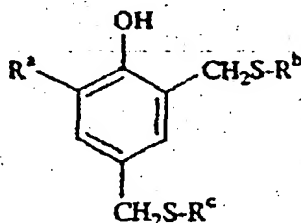
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(54) Title: LIQUID CURABLE RESIN COMPOSITION FOR OPTICAL FIBERS



(1)

(57) Abstract: A liquid curable resin composition comprising for optical fibers (A) a urethane (meth)acrylate oligomer in particular an oligomer comprising a polyether backbone, (B) an unsaturated polymerizable compound, (C) a photoinitiator, and (D) an antioxidant which causes the cured coating to exhibit a yellowing index after five days exposure of less than 5, and a Young's modulus retention rate of more than 70 % after aging for 30 days at 100 °C. In particular, component D can be a compound shown by the following formula (1), wherein R^a represents a hydrogen atom or an alkyl group having 1-4 carbon atoms and R^b and R^c individually represent alkyl groups having 1-12 carbon atoms, or 2-tert-butyl-6-(3'-tert-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate.

LIQUID CURABLE RESIN COMPOSITION FOR OPTICAL FIBERS5 Field of the Invention

The present invention relates to a liquid curable resin composition exhibiting excellent light resistance, suitable as a coating material for optical fibers, optical fiber ribbons, and the like, and to a cured product thereof.

10 Description of related Art

In the fabrication of optical fibers, a resin coating is applied for protection and reinforcement over glass fiber produced by spinning molten glass. As such a resin coating, a structure consisting of a primary flexible coating layer formed on the surface of optical fiber and a secondary rigid coating layer applied thereon is known. Optical fiber ribbons in which a number of optical fibers provided with a resin coating are bundled side by side in a plane using a bundling material are also well known. A resin composition for forming the primary coating layer is called a primary material, a resin composition for forming the secondary coating layer is called a secondary material, and a resin composition used for the bundling material for optical fiber ribbons is called a ribbon matrix material. As a method of applying these resins, a method of applying a liquid curable resin composition and then curing the composition using heat or light, in particular, ultraviolet rays has been widely used.

Since optical fibers are used over a long period of time, coating materials used therefor must exhibit only a slight change in characteristics over a long period of time.

Coated optical fibers and optical fiber ribbons are often stored before and after shipment in a warehouse under fluorescent light. This causes the color of the coating materials to become yellowish during storage. The cause of such a change in color is considered to be related to the presence of the hindered phenol-type antioxidant which is added to ensure heat stability of the cured product. However, antioxidants which do not impair the color stability have not yet been known.

An object of the present invention is to provide a liquid curable resin composition for optical fibers of which the cured product exhibits excellent heat stability when used as a coating material for optical fibers or optical fiber ribbons and small changes in color when stored under fluorescent light.

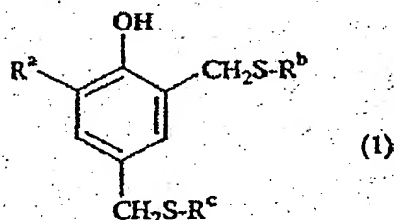
A further object of the invention is to provide coated optical fibers and ribbon structures having at least one coating that exhibits excellent heat stability and small change in color when stored under fluorescent light, as these products are particularly useful in the industry.

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Summary of the invention

The present inventors have found that a liquid curable resin composition of which the cured product exhibits heat stability and color stability under fluorescent light can be obtained by combining a urethane (meth)acrylate oligomer, an unsaturated polymerizable compound, a photoinitiator, and a suitable antioxidant. This finding has led to the completion of the present invention.

The present invention provides coated optical fibers and ribbon structures having at least one coating layer, which coating before curing is comprising (A) a urethane (meth)acrylate oligomer comprising a polyether backbone (B) an unsaturated polymerizable compound, (C) a photoinitiator and an antioxidant (D) in which the cured composition as a 200 μm thick film exhibits a yellowing index after five days exposure of less than 5, and a Youngs modulus retention rate of more than 70% after aging for 30 days at 100°C. Furthermore, the present invention provides a liquid curable resin composition comprising (A) a urethane (meth)acrylate oligomer, (B) an unsaturated polymerizable compound, (C) a photoinitiator, and (D) a compound shown by the following formula (1),



wherein R^a represents a hydrogen atom or an alkyl group having 1-4 carbon atoms and R^b and R^c individually represent alkyl groups having 1-12 carbon atoms, or 2-tert-butyl-6-(3'-tert-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate, and a cured product obtained by photocuring the composition.

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Detailed description of the Invention

The urethane (meth)acrylate (A) used in the present invention is produced by reacting a polyol, diisocyanate, and (meth)acrylate containing a hydroxyl group. Specifically, the urethane (meth)acrylate (A) is produced by
5 reacting isocyanate groups of a diisocyanate with hydroxyl groups of a polyol and a (meth)acrylate containing a hydroxyl group. The polyol is generally denoted as constituting the backbone of the urethane oligomer. Hence, if the polyol is e.g. a polyether diol, the urethane oligomer is said to comprise a polyether backbone.

As a method of reacting these compounds, a method of reacting
10 a polyol, diisocyanate, and (meth)acrylate containing a hydroxyl group all together; a method of reacting a polyol with a diisocyanate, and then reacting the resulting product with a (meth)acrylate containing a hydroxyl group; a method of reacting a diisocyanate with a (meth)acrylate containing a hydroxyl group, and then reacting the resulting product with a polyol; a method of reacting a
15 diisocyanate with a (meth)acrylate containing a hydroxyl group, reacting the resulting product with a polyol, and further reacting the resulting product with a (meth)acrylate containing a hydroxyl group; and the like can be given.

As examples of a polyol compound used in this reaction, polyether diols obtained by ring-opening polymerization of one ion-polymerizable cyclic
20 compound such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, and polydecamethylene glycol, polyether diols obtained by ring-opening copolymerization of two or more ion-polymerizable cyclic compounds, and the like can be given. As examples of ion-polymerizable cyclic compounds, cyclic ethers
25 such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, oxetane, 3,3-dimethyloxetane, 3,3-bischloromethyloxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrin, glycidyl methacrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide,
30 vinylloxetane, vinyltetrahydrofuran, vinylcyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl benzoate can be given. Polyether diols obtained by ring-opening copolymerization of these ion-polymerizable cyclic compounds and cyclic imines such as ethyleneimine, cyclic lactonic acids such as β -propylactone and glycolic acid lactide, or dimethylcyclopolsiloxanes can also be

used. As examples of specific combinations of two or more ion-polymerizable cyclic compounds, combinations of tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyltetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, butene-1-oxide and ethylene oxide, a ternary copolymer of tetrahydrofuran, butene-1-oxide, and ethylene oxide, and the like can be given. The ring-opening copolymers of the ion-polymerizable cyclic compounds may be either a random copolymer or a block copolymer.

Examples of commercially available products of these polyether diols include PTMG650, PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Corp.), EXCENOL 1020, 2020, 3020, PREMINOL PML-4002, PML-5005 (manufactured by Asahi Glass Co., Ltd.), UNISAFE DC1100, DC1800, DCB1000 (manufactured by Nippon Oil and Fats Co., Ltd.), PPTG1000, PPTG2000, PPTG4000, PTG400, PTG650, PTG1000, PTG2000, PTG-L1000, PTG-L2000 (manufactured by Hodogaya Chemical Co., Ltd.), Z-3001-4, Z-3001-5, PBG2000 (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), ACCLAIM 2200, 2220, 3201, 3205, 4200, 4220, 8200, 12200 (manufactured by Lyondell), and the like can be given.

The above polyether diols are preferable as the polyol compound. In addition, a polyester diol, polycarbonate diol, polycaprolactone diol, and the like can also be used. These diols may be used in combination with the polyether diols. The polyether diol is used preferably in at least 20 wt.% of the diol total weight, more preferably at least 40 wt.%. In another embodiment of the present invention, the polyether diol is used in an amount of more than 80wt.% of the diol total weight. The structural units of these compounds may be polymerized by a random polymerization, block polymerization, or graft polymerization without specific limitations.

As examples of polyester diols, polyester polyols obtained by reacting a polyhydric alcohol such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, and 2-methyl-1,8-octanediol with a polybasic acid such as phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, and sebacic acid, and the like can be given. As commercially available products of such polyester diols, Kurapol P-1010, P-2010, F-1010, F-

2010, PMIPA-2000, PKA-A, PKA-A2, PNA-2000 (manufactured by Kuraray Co., Ltd.), and the like can be given.

As examples of polycarbonate diols, polycarbonate of polytetrahydrofuran, polycarbonate of 1,6-hexanediol, and the like can be given.

5 As examples of commercially available products of such polycarbonate diols, Nippolan 980, 981, 982, 983 (manufactured by Nippon Polyurethane Industry Co., Ltd.), Duracarb 120, 122, 124, 140, 142 (manufactured by PPG), PLACCEL CD 205, 208, 210, 220, 205PL, 208PL, 210PL, 220PL, 205HL, 208HL, 210HL, 220HL (manufactured by Daicel Chemical Industries, Ltd.), and the like can be given.

10 As examples of polycaprolactone diols, polycaprolactone diols obtained by reacting ϵ -caprolactone and dihydric diols such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, and 1,4-butanediol can be given. As
15 commercially available products of these diols, PLACCEL 205, L205AL, 212, L212AL, 220, L220AL (manufactured by Daicel Chemical Industries, Ltd.), and the like can be given.

Diols other than those mentioned above can also be used. As examples of other polyols, ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-
20 pentanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, β -methyl- δ -valerolactone, hydroxy-terminal polybutadiene, hydroxy-terminal hydrogenated polybutadiene, castor oil-modified polyol, diol terminated compound of polydimethylsiloxane, polydimethylsiloxanecarbitol-modified polyol, and the like can be given.

25 In addition to the above diols, diamines may be used in combination with the diols having a polyoxyalkylene structure. As examples of diamines, ethylenediamine, tetramethylenediamine, hexamethylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylmethane, diamines containing a hetero atom, polyether diamines, and the like can be given.

30 The number average molecular weight of these polyols is preferably from 50 to 15,000, and particularly preferably from 100 to 8,000.

The following compounds may be used as polyols having a cyclic structure. Examples include alkylene oxide addition diol of bisphenol A, alkylene oxide addition diol of bisphenol F, hydrogenated bisphenol A,

hydrogenated bisphenol F, alkylene oxide addition diol of hydrogenated bisphenol A, alkylene oxide addition diol of hydrogenated bisphenol F, alkylene oxide addition diol of hydroquinone, alkylene oxide addition diol of naphthohydroquinone, alkylene oxide addition diol of anthrahydroquinone, 1,4-cyclohexane diol, and its alkylene oxide addition diol, tricyclodecane diol, tricyclodecanedimethanol, pentacyclopentadecane diol, pentacyclopentadecanedimethanol, and the like. Of these, alkylene oxide addition diol of bisphenol A and tricyclodecanedimethanol are preferable. As commercially available products of these polyols, Uniol DA400, DA700, DA1000, DB400 (manufactured by Nippon Oil and Fats Co., Ltd.), tricyclodecanedimethanol (manufactured by Mitsubishi Chemical Corp.), and the like can be given. Polyols having a cyclic structure are used preferably in secondary coatings, matrix materials and inks.

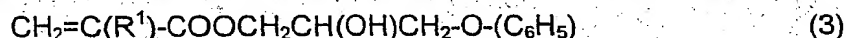
Examples of a diisocyanate include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, bis(2-isocyanate ethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, lysine diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, tetramethyxylylene diisocyanate, 2,5-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, 2,6-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, and the like. Of these, 2,4-tolylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, and methylenebis(4-cyclohexylisocyanate) are preferable. Aliphatic isocyanates are particularly preferred because of a reduced tendency for yellowing.

As examples of a (meth)acrylate containing a hydroxyl group, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl (meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol

penta(meth)acrylate, and (meth)acrylates shown by the following formula (2) or (3) can be given:



5



wherein R^1 represents a hydrogen atom or a methyl group and n is an integer from 1 to 15.

10

Compounds obtained by the addition reaction of (meth)acrylic acid and a compound containing a glycidyl group such as alkyl glycidyl ether, allyl glycidyl ether, and glycidyl (meth)acrylate can also be used. Of these (meth)acrylates containing a hydroxyl group, 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate are particularly preferable.

15

The proportion of the polyol, diisocyanate, and (meth)acrylate containing a hydroxyl group is determined so that isocyanate groups in the diisocyanate and a hydroxyl group in the (meth)acrylate containing a hydroxyl group are 1.1 to 3 equivalents and 0.2 to 1.5 equivalents respectively for one equivalent of hydroxyl groups in the polyol. It is preferable that the equivalent of hydroxyl groups in the polyol and (meth)acrylate containing a hydroxyl group be almost equal to the equivalent of isocyanate groups in the diisocyanate.

20

Part of the (meth)acrylate containing a hydroxyl group may be replaced by compounds having a functional group which can be added to an isocyanate group. For example, γ -mercaptopotrimethoxysilane, γ -aminotrimethoxysilane, and the like can be used. Use of these compounds improves adhesion to substrates such as glass.

25

In the reaction of these compounds, it is preferable to use a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate, dibutyltin dilaurate, triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane in an amount from 0.01 to 1 part by weight for 100 parts by weight of the reactant. The reaction is carried out at 10-90°C, and preferably at 30-80°C. The proportion of the urethane (meth)acrylate oligomer (A) is 10-90 wt% (hereinafter indicated by simply "%") of the composition. It is particularly preferable that the proportion of the urethane (meth)acrylate

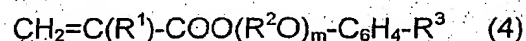
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oligomer (A) be 20-70% to ensure excellent applicability when applying the composition to optical fibers, and flexibility and long-term reliability of the cured coating.

A urethane (meth)acrylate obtained by reacting 1 mol of the
5 diisocyanate with 2 mols of the (meth)acrylate containing a hydroxyl group may be added to the liquid curable resin composition of the present invention. As examples of such a urethane (meth)acrylate, a reaction product of hydroxyethyl (meth)acrylate, 2,5-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, and 2,6-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, a reaction product of hydroxyethyl
10 (meth)acrylate and 2,4-tolylene diisocyanate, a reaction product of hydroxyethyl (meth)acrylate and isophorone diisocyanate, a reaction product of hydroxypropyl (meth)acrylate and 2,4-tolylene diisocyanate, a reaction product of hydroxypropyl (meth)acrylate and isophorone diisocyanate, and the like can be given.

As examples of the unsaturated polymerizable compound (B)
15 used in the liquid curable resin composition of the present invention, vinyl group-containing lactams such as N-vinylpyrrolidone and N-vinylcaprolactam, alicyclic structure-containing (meth)acrylates such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, and cyclohexyl (meth)acrylate, benzyl
20 (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, acryloylmorpholine, vinylimidazole, vinylpyridine, and the like can be given. Further examples include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxy butyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl
25 (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl
30 (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxy polyethylene glycol (meth)acrylate, methoxy
35 polypropylene glycol (meth)acrylate, diacetone (meth)acrylamide, isobutoxymethyl

- (meth)acrylamide, N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, hydroxybutyl vinyl ether, lauryl vinyl ether, cetyl-vinyl ether, 2-ethylhexyl vinyl ether, a compound shown by the following formula (4), and the like:



- wherein R^1 represents a hydrogen atom or a methyl group, R^2 represents an alkylene group having 2-6, and preferably 2-4 carbon atoms, R^3 represents a hydrogen atom or an alkyl group having 1-12, and preferably 1-9 carbon atoms, and m is an integer from 0 to 12, and preferably from 1 to 8.

- As examples of commercially available products of the unsaturated polymerizable compounds, Aronix M-101, M-102, M-111, M-113, M-114, M-117 (manufactured by Toagosei Co., Ltd.), Viscoat LA, STA, IBXA, 2-MTA, #192, #193 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), NK Ester AMP-10G, AMP-20G, AMP-60G (manufactured by Shin-Nakamura Chemical Co., Ltd.), Light Acrylate L-A, S-A, IB-XA, PO-A, PO-200A, NP-4EA, NP-8EA (manufactured by Kyoisha Chemical Co., Ltd.), FA-511, FA-512A, FA-513A (manufactured by Hitachi Chemical Co., Ltd.), and the like can be given.

- Polyfunctional compounds can be given as examples of the unsaturated polymerizable compound (B). Examples of unsaturated polymerizable polyfunctional compounds include trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropanetrioxethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, di(meth)acrylate of diol of an ethylene oxide or propylene oxide addition product of bisphenol A, di(meth)acrylate of diol of an ethylene oxide or propylene oxide addition product of hydrogenated bisphenol A, epoxy(meth)acrylate obtained by the addition of (meth)acrylate to diglycidyl ether of bisphenol A, triethylene glycol divinyl ether, and the like.

As examples of commercially available products of the unsaturated polymerizable polyfunctional compounds, Yupimer UV SA1002, SA2007 (manufactured by Mitsubishi Chemical Corp.), Viscoat #195, #215, #230, #260, #700 (manufactured by Osaka Organic Chemical Industry, Ltd.), KAYARAD
5 HDDA (manufactured by Nippon Kayaku Co., Ltd.), ARONIX M-210, M-215, M-315 (manufactured by Toagosei Co., Ltd.), and the like can be given. Of these, tricyclodecanedimethanol diacrylate (Yupimer UV SA1002) and Viscoat #230 and #700 are preferable.

The proportion of the unsaturated polymerizable compound (B)
10 is preferably 15-80%, and particularly preferably 20-70% of the composition. If the proportion is less than 15%, applicability of the composition may be impaired due to increased viscosity. Moreover, toughness of the cured product decreases and cure shrinkage rate increases. If the proportion exceeds 80%, the curing rate of the composition decreases.

As examples of the photoinitiator (C),
1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone,
4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone,
20 benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyldiphenylphosphine oxide,
25 bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, and the like can be given.

As examples of commercially available products of the photoinitiator (C), Irgacure 184, 261, 369, 500, 651, 819, 907, 1700, 1850, 2959, CGI-403, Darocur 1173 (manufactured by Ciba Specialty Chemicals Co., Ltd.),
30 Lucirin TPO (manufactured by BASF), and the like can be given. Of these, Irgacure 184, 369, 651, 907, 1700, 1800, 1850, and Lucirin TPO are preferable with Lucirin TPO being particularly preferable.

The proportion of the photoinitiator (C) is preferably 0.01-10%, and particularly preferably 0.01-4% of the composition.

35 The component (D) used in the liquid curable resin composition

of the present invention is a compound suitable to impair most useful stability characteristics. Stability characteristics are exemplified by a combination of heat stability and stability under fluorescent lights; the cured coating exhibits preferably a yellowing index after five days exposure of fluorescent light of less than 5, and a
5 Youngs modulus retention rate of more than 70% after aging for 30 days at 100°C. Coated optical fibers having a cured coating with said properties are most useful, as the coated fibers have excellent storage stability. The test methods are fully described in the experimental fully described in the experimental section. Preferably, the Yellowing index is less than 4. Preferably, the Youngs modulus
10 retention rate is about 80% or more, particularly preferred about 90% or more.

Specific compound, useful as component D of the present invention are shown by the formula (1) or 2-tert-butyl-6-(3'-tert-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate. In the formula (1), R^a, which is an alkyl group having 1-4 carbon atoms, is preferably a methyl group. R^b and R^c are
15 preferably alkyl groups having 5-12, and preferably 6-12 carbon atoms. 4,6-Bis(octylthiomethyl)-o-cresol, a compound shown by the formula (1) provided that R^a is a methyl group and both R^b and R^c are alkyl groups having eight carbon atoms, is commercially available as Irganox 1520, 1520L, and 1520LR (manufactured by Ciba Specialty Chemicals Co., Ltd.). 2-Tert-butyl-6-(3'-tert-butyl-
20 5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate is commercially available as Sumilizer GM (manufactured by Sumitomo Chemical Co., Ltd.).

The proportion of the component (D) is 0.01-3%, preferably 0.03-1%, and particularly preferably 0.05-0.5% of the composition for ensuring heat stability and color stability under fluorescent light.

25 In addition to the above components, other curable oligomers or polymers, reactive dilutents, or other additives may be added to the liquid curable resin composition of the present invention, insofar as the characteristics of the liquid curable resin composition are not impaired.

As examples of other curable oligomers or polymers, polyester
30 (meth)acrylate, epoxy (meth)acrylate, polyamide (meth)acrylate, a siloxane polymer having a (meth)acryloyloxy group, a reactive polymer obtained by reacting acrylic acid and a copolymer of glycidyl methacrylate and other vinyl monomers, and the like can be given.

Amines may be added to the liquid curable resin composition to
35 prevent generation of hydrogen gas, which causes transmission loss in optical

fibers. As examples of amines, diethylamine, isopropylamine, dibutylamine, ethanolamine, diethanolamine, and the like can be given.

Other additives such as coloring agents, UV absorbers, light stabilizers, silane coupling agents, heat polymerization inhibitors, leveling agents, surfactants, preservatives, plasticizers, lubricants, solvents, fillers, wettability improvers, and coating surface improvers may be added in addition to the above components. As examples of UV absorbers, benzophenone-type UV absorbers such as 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, and 2-hydroxy-4-n-dodecyloxybenzophenone, benzotriazole-type UV absorbers such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole and 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole, commercially available products such as Tinuvin P, 234, 320, 326, 327, 328, 329, 213 (manufactured by Ciba Specialty Chemicals Co., Ltd.), Seesorb 101, 102, 103, 712, 704 (manufactured by Shipro Kasei Kaisha, Ltd.), Sumisorb 110, 130, 140 (manufactured by Sumitomo Chemical Industries Co., Ltd.), and the like can be given. As examples of silane coupling agents, γ -aminopropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, and γ -(meth)acryloxypropyltrimethoxysilane, commercially available products such as SH6062, SH6030 (manufactured by Toray-Dow Corning Silicone Co. Ltd.), KBM 403, 503, 803, 903, 5103 (manufactured by Shin-Etsu Chemical Co., Ltd.), and the like can be given.

The viscosity of the liquid curable resin composition of the present invention is 200-20,000 mPa·s/25°C, and preferably 2000-15,000 mPa·s/25°C. When the liquid curable resin composition of the present invention is used as a secondary material or ribbon matrix material for optical fibers, the Young's modulus after curing is preferably 100-2500 MPa. When used as a primary material for optical fibers, the Young's modulus after curing is preferably 0.5-3 MPa. The cure speed preferably is about 0.5 J/cm² or less, more preferably about 0.3 J/cm² or less. The cure speed is defined as the energy applied to achieve 90% of the ultimate modulus. The water absorption of the coatings preferably is less than 5 wt.%.

The optical fiber, preferably glass fiber, is drawn from a preform and has a diameter of about 125 μ m. The fiber is coated with a primary and a secondary coating before the glass is touched. Both coatings, generally are 25-30 μ m thick, but this can be chosen differently, e.g. 5 μ m-500 μ m. The coated

optical fiber generally needs to be colored to enable identification in the field. Thus, an ink layer can be applied on the coated optical fiber, or the secondary coating can contain color identification means (pigments, dyes). The coated and colored optical fibers can be used in cabling for example for loose tube cables, or ribbon cables. In a ribbon structure, used in the second type of cable, multiple coated optical fibers (generally 2, 4, 8, 12 up to 24) are bonded together, generally in a plane. Bonding can take place through edge-bonding or encasing. Sometimes two or more matrix coatings are applied. Another type of matrix material is used to bind a plurality of ribbons either in a plane, or stacked. These materials are also called bundling materials. For any of these coating layers, the cured coating of the present invention is advantageous.

The liquid curable resin composition of the present invention is cured using heat and/or radiation. Radiation used herein includes infrared rays, visible rays, ultraviolet rays, X-rays, electron beams, α -rays, β -rays, γ -rays, and the like. UV and UV-vis radiation is particularly preferred.

EXAMPLES

The present invention will be described in more detail by examples, which are not intended to be limiting of the present invention.

Synthesis Example 1 (Synthesis of urethane acrylate oligomer)

A reaction vessel equipped with a stirrer was charged with 117.12 g of isophorone diisocyanate, 0.24 g of 2,6-di-t-butyl-p-cresol, 0.08 g of phenothiazine, and 0.40 g of dibutyltin dilaurate. 37.08 g 2-hydroxyethyl acrylate was added dropwise to the mixture at 30°C or lower. After the addition, the mixture was allowed to react at 30°C for 40 minutes. The mixture was then heated to 45°C and allowed to react for a further one hour. Then, 844.68 g of ring-opening copolymer diol of ethylene oxide and butylene oxide (weight ratio: 25/75) with a number average molecular weight of 2300 and 0.40 g of dibutyltin dilaurate were added to the mixture. The mixture was allowed to react at 50°C for one hour. The mixture was then further allowed to react at 70°C. The reaction was terminated when the residual isocyanate concentration was 0.05 wt% or less to obtain a urethane acrylate oligomer (this oligomer is referred to as "UA-1").

Synthesis Example 2 (Synthesis of urethane acrylate oligomer)

A reaction vessel equipped with a stirrer was charged with 898.07 g of polypropylene glycol with a number average molecular weight of 4000 ("ACCLAIM 4200" manufactured by Lyondell), 74.76 g of isophorone diisocyanate, 0.24 g of 2,6-di-t-butyl-p-cresol, and 0.08 g of phenothiazine. The mixture was cooled to 15°C while stirring. After the addition of 0.80 g of dibutyltin dilaurate, the mixture was slowly heated to 35°C for one hour while stirring. Then, the mixture was allowed to react at 50°C. After the residual isocyanate concentration was decreased to 0.97 wt% or less (of the total amount of the reactants), 26.04 g of 2-hydroxybutyl acrylate was added. The mixture was allowed to react at about 60°C while stirring. The reaction was terminated when the residual isocyanate concentration was 0.1 wt% or less to obtain a urethane acrylate oligomer (this oligomer is referred to as "UA-2").

Example 1

A reaction vessel equipped with a stirrer was charged with 65 parts by weight of the urethane acrylate oligomer UA-1 obtained in Synthesis Example 1, 26 parts by weight of nonylphenol EO-modified acrylate ("Aronix M-113" manufactured by Toagosei Co., Ltd.), 8 parts by weight of N-vinylcaprolactam (manufactured by ISP Japan, Ltd.), 1 part by weight of 1,6-hexanediol diacrylate ("Viscoat #230" manufactured by Osaka Organic Chemical Industry, Ltd.), and 1.2 parts by weight of 2,4,6-trimethylbenzoyldiphenylphosphine oxide ("Lucirin TPO" manufactured by BASF). The mixture was stirred at 50°C to prepare a homogeneous solution. Then, 0.1 part by weight of diethylamine and 1.0 part by weight of γ -mercaptopropyltrimethoxysilane ("SH6062" manufactured by Toray-Dow Corning Silicone Co., Ltd.) were added to the mixture. 0.3 part by weight of 4,6-bis(octylthiomethyl)-o-cresol ("Irganox 1520L" manufactured by Ciba Specialty Chemicals Co., Ltd.) was added to the mixture to obtain a liquid curable resin composition.

Example 2

A liquid curable resin composition was prepared in the same manner as in Example 1 except for using 2-tert-butyl-6-(3'-tert-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate ("Sumilizer GM" manufactured by Sumitomo Chemical Co., Ltd.) instead of 4,6-bis(octylthiomethyl)-o-cresol.

Example 3

A reaction vessel equipped with a stirrer was charged with 63 parts by weight of the urethane acrylate oligomer UA-2 obtained in Synthesis Example 2, 12 parts by weight of nonylphenol EO-modified acrylate ("Aronix M-113" manufactured by Toagosei Co., Ltd.), 8 parts by weight of N-vinylcaprolactam (manufactured by ISP Japan, Ltd.), 15 parts by weight of isobornyl acrylate ("IBXA" manufactured by Osaka Organic Chemical Industry Co., Ltd.), 2 parts by weight of 1,6-hexanediol diacrylate ("Viscoat #230" manufactured by Osaka Organic Chemical Industry, Ltd.), 1.2 parts by weight of 2,4,6-trimethylbenzoyldiphenylphosphine oxide ("Lucirin TPO" manufactured by BASF), and 0.15 part by weight of 2-hydroxy-4-methoxybenzophenone ("Seesorb 101" manufactured by Shipro Kasei Kaisha, Ltd.). The mixture was stirred at 50°C to prepare a homogeneous solution. Then, 0.1 part by weight of diethylamine and 1.0 part by weight of γ -mercaptopropyltrimethoxysilane were added to the mixture. 0.3 part by weight of 4,6-bis(octylthiomethyl)-o-cresol ("Irganox 1520L" manufactured by Ciba Specialty Chemicals Co., Ltd.) was added to the mixture to obtain a liquid curable resin composition.

Comparative Example 1

A liquid curable resin composition was prepared in the same manner as in Example 1 except that 4,6-bis(octylthiomethyl)-o-cresol was not added.

Comparative Example 2

A liquid curable resin composition was prepared in the same manner as in Example 1 except for using pentaerythritoltetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] ("Irganox 1010" manufactured by Ciba Specialty Chemicals Co., Ltd.) instead of 4,6-bis(octylthiomethyl)-o-cresol.

Comparative Example 3

A liquid curable resin composition was prepared in the same manner as in Example 1 except for using thiodiethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] ("Irganox 1035" manufactured by Ciba Specialty Chemicals Co., Ltd.) instead of 4,6-bis(octylthiomethyl)-o-cresol.

Comparative Example 4

A liquid curable resin composition was prepared in the same manner as in Example 1 except for using benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-C₇-C₉ branched alkyl ester ("Irganox 1135" manufactured by Ciba Specialty Chemicals Co., Ltd.) instead of 4,6-bis(octylthiomethyl)-o-cresol.

Comparative Example 5

A liquid curable resin composition was prepared in the same manner as in Example 1 except for using hexamethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] ("Irganox 259" manufactured by Ciba Specialty Chemicals Co., Ltd.) instead of 4,6-bis(octylthiomethyl)-o-cresol.

Comparative Example 6

A liquid curable resin composition was prepared in the same manner as in Example 1 except for using 4,4'-thio-bis-(3'-methyl-6-tert-butylphenol) ("Sumilizer WX-R" manufactured by Sumitomo Chemical Industries Co., Ltd.) instead of 4,6-bis(octylthiomethyl)-o-cresol.

Comparative Example 7

A liquid curable resin composition was prepared in the same manner as in Example 3 except that 4,6-bis(octylthiomethyl)-o-cresol was not added.

Comparative Example 8

A liquid curable resin composition was prepared in the same manner as in Example 3 except for using thiodiethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] ("Irganox 1035" manufactured by Ciba Specialty

Chemicals Co., Ltd.) instead of 4,6-bis(octylthiomethyl)-o-cresol.

Comparative Example 9

- 5 A liquid curable resin composition was prepared in the same manner as in Example 3 except for using benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-C₇-C₉ branched alkyl ester ("Irganox 1135" manufactured by Ciba Specialty Chemicals Co., Ltd.) instead of 4,6-bis(octylthiomethyl)-o-cresol.

10 Test Examples

The light resistance and heat stability of the cured products of the compositions obtained in Examples and Comparative Examples were evaluated.

15 (1) Fluorescent light resistance test

- The liquid compositions were applied to a glass plate using an applicator with a thickness of 254 μm . The applied compositions were irradiated with ultraviolet rays in a nitrogen atmosphere using a 3.5 kW metal halide lamp ("SMX-3500/F-OS", manufactured by ORC Co., Ltd.) at a dose of 0.1 J/cm² to
20 obtain cured films with a thickness of about 130 μm . The cured films on the glass plate were irradiated with fluorescent light at a temperature of 23°C and relative humidity of 50%. As a fluorescent lamp, "FL20SSN/18" manufactured by Toshiba Corporation was used. Illuminance at the surface of the cured films was 1200 lx. The degree of yellowing of the cured films before irradiation of fluorescent light
25 and after irradiation for a predetermined period of time were evaluated by a yellowness index (YI) using a colorimeter ("SZ-Σ80 spectrophotometer" manufactured by Nippon Denshoku Industries Co., Ltd.). The smaller the YI value, the less the degree of yellowing.

30 (2) Heat stability test

The heat stability of the cured products of the compositions obtained in Examples and Comparative Examples was evaluated. The liquid compositions were applied to a glass plate using an applicator with a thickness of 381 μm . The applied compositions were irradiated with ultraviolet rays in air using

a 3.5 kW metal halide lamp ("SMX-3500/F-OS", manufactured by ORC Co., Ltd.) at a dose of 0.5 J/cm^2 to obtain cured films. The cured films removed from the glass plate were irradiated with ultraviolet rays from the other side at a dose of 0.5 J/cm^2 . The thickness of the resulting films was about $200 \mu\text{m}$. The cured films
5 were allowed to stand for 12 hours or more at a temperature of 23°C and relative humidity of 50%. The initial Young's modulus of the cured films was then measured. The cured films were allowed to stand in an oven at 100°C for 30 days. The Young's modulus of these cured films was then measured. Heat stability was evaluated by calculating the variation between the initial Young's modulus and the
10 Young's modulus after heating.

Measurement of Young's modulus

The cured films were cut into sheets with a width of 6 mm. The modulus of elasticity of the sheets was measured using a tensile tester. The
15 tensile rate was 1 mm/minute and the distance between chucks was 25 mm. The Young's modulus was calculated by dividing the load at 2.5% elongation by the cross section of the test specimen and 0.025. The results are shown in Table 1.

[Table 1]

	Example			Comparative Example			Example			Comparative Example		
	1	2	3	4	5	6	7	8	9	10	11	12
UA-1	65	65	65	65	65	65	-	-	-	63	63	63
UA-2	26	26	26	26	26	26	12	12	12	12	12	12
Polyoxyethylene nonyl phenyl ether acrylate	8	8	8	8	8	8	8	8	8	8	8	8
N-vinylcaprolactam	-	-	-	-	-	-	15	15	15	15	15	15
Isobornyl acrylate	1	1	1	1	1	1	2	2	2	2	2	2
1,6-Hexanediol diacrylate	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
2,4,6-Trimethylbenzoyldiphenylphosphine oxide	0.3	-	-	-	-	-	0.3	-	-	-	-	-
Irganox 1520L	-	0.3	-	-	-	-	-	-	-	-	-	-
Sumilizer GM	-	-	-	-	-	-	-	-	-	-	-	-
Irganox 1010	-	-	-	-	-	-	-	-	-	-	-	-
Irganox 1035	-	-	-	-	-	-	-	-	-	-	-	-
Irganox 1135	-	-	-	-	-	-	-	-	-	-	-	-
Irganox 259	-	-	-	-	-	-	-	-	-	-	-	-
Sumilizer WX-R	-	-	-	-	-	-	-	-	-	-	-	-
2-Hydroxy-4-methoxybenzophenone	-	-	-	-	-	-	0.15	0.15	0.15	0.15	0.15	0.15
Diethylamine	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
γ -Mercaptopropyltrimethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Fluorescent light resistance (degree of yellowing)	2	2	2	2	2	2	1	1	1	1	1	1
YI (initial value)	3	4	2	8	11	6	3	2	8	9	9	9
YI (after five days)												
Heat stability (100°C)												
Young's modulus (MPa, initial value)	1.0	1.0	1.0	1.0	1.0	1.0	1.2	1.2	1.2	1.2	1.2	1.2
Young's modulus (MPa, after 30 days)	0.9	0.9	0.3	0.9	0.8	0.8	1.1	1.1	1.1	1.1	1.1	1.0
Young's modulus retention rate (%)	90	90	30	90	80	80	92	92	92	92	92	83

Irganox 1520L:

4,6-bis(octylthiomethyl)-o-cresol (manufactured by Ciba Specialty Chemicals Co., Ltd.)

Sumilizer GM:

- 5 2-Tert-butyl-6-(3'-tert-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate (manufactured by Sumitomo Chemical Co., Ltd.)

Irganox 1010:

Pentaerythritoltetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (manufactured by Ciba Specialty Chemicals Co., Ltd.)

- 10 Irganox 1035:

Thiodiethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (manufactured by Ciba Specialty Chemicals Co., Ltd.)

Irganox 1135:

- 15 Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-C₇-C₉ branched alkyl ester (manufactured by Ciba Specialty Chemicals Co., Ltd.)

Irganox 259:

Hexamethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (manufactured by Ciba Specialty Chemicals Co., Ltd.)

Sumilizer WX-R:

- 20 4,4'-Thio-bis-(3-methyl-6-tert-butyl-phenol) (manufactured by Sumitomo Chemical Co., Ltd.)

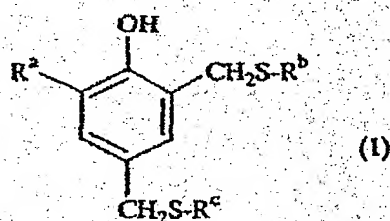
25 As is clear from Table 1, the cured products of the liquid curable resin compositions comprising the component (D) exhibited excellent stability in fluorescent light and superior heat stability.

Effect of the Invention

- 30 The cured products made from the liquid curable resin composition of the present invention exhibit excellent light resistance and superior heat stability. The resin composition is suitable for use as a coating material for optical fibers.

CLAIMS

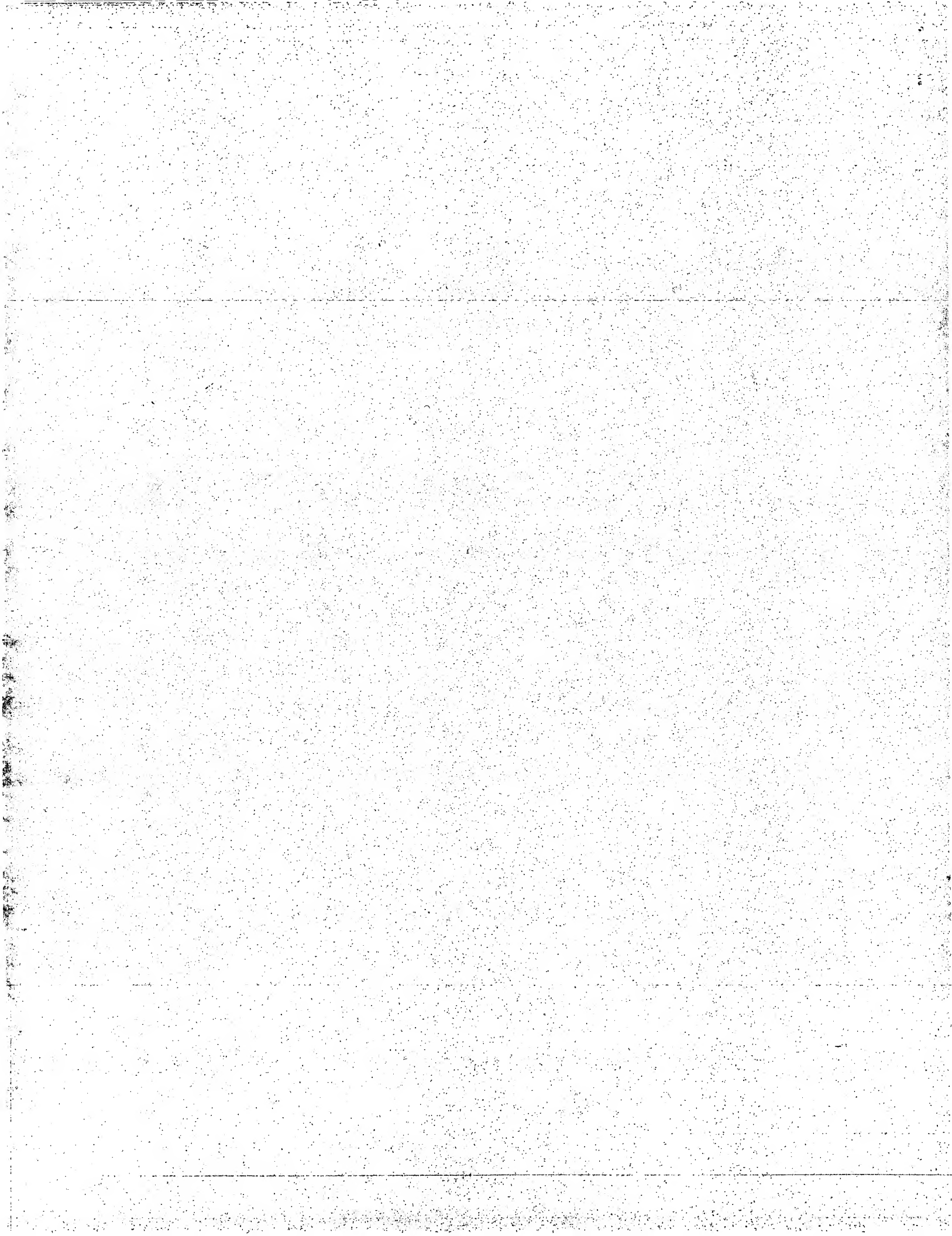
1. Coated optical fiber or ribbon structure having at least one coating layer, which coating before curing comprises (A) a urethane (meth)acrylate oligomer comprising a polyether backbone (B) an unsaturated polymerizable compound, (C) a photoinitiator and an antioxidant (D) in which the cured composition as a 200 μm thick film exhibits a yellowing index after five days exposure of less than 5, and a Youngs modulus retention rate of more than 70% after aging for 30 days at 100°C.
2. A liquid curable resin composition for coating optical fibers comprising (A) a urethane (meth)acrylate oligomer, (B) an unsaturated polymerizable compound, (C) a photoinitiator, and (D) a compound shown by the following formula (1),



- wherein R^a represents a hydrogen atom or an alkyl group having 1-4 carbon atoms and R^b and R^c individually represent alkyl groups having 1-12 carbon atoms, or 2-tert-butyl-6-(3'-tert-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate.
3. The liquid curable resin composition according to claim 2 wherein R^a is a methyl group and R^b and R^c are octyl groups.
 4. The liquid curable resin composition according to claim 2 or 3, wherein the urethane (meth)acrylate oligomer (A) comprises a polyether backbone.
 5. Liquid curable resin composition for coating optical fibers comprising (A) a urethane (meth)acrylate oligomer comprising a polyether backbone (B) an unsaturated polymerizable compound, (C) a photoinitiator and an antioxidant (D) in which the cured composition as a 200 μm thick film exhibits a yellowing index after five days exposure of less than 5, and a Youngs modulus retention rate of more than 70% after aging for 30 days

at 100°C.

6. The liquid curable resin composition according to any one of claims 1 to 5, wherein the photoinitiator (C) is 2,4,6-trimethylbenzoyl-diphenylphosphine oxide.
- 5 7. Use of a liquid curable resin composition according to any one of claims 2 to 6, for coating optical fibers.
8. A cured coating layers obtained by photocuring the liquid curable resin composition according to any one of claims 2 to 6.
9. A coated optical fiber or ribbon structure or cured coating layer of claim 1 or 8 wherein the coating layer is a primary coating on an optical glass fiber.
- 10 10. A coated optical fiber or ribbon structure or cured coating layer of claim 1 or 8 wherein the coating layer is a secondary coating on a primary coated optical glass fiber.
- 15 11. A coated optical fiber or ribbon structure or cured coating layer of claim 1 or 8 wherein the coating layer is a matrix material binding a plurality of coated optical glass fibers.



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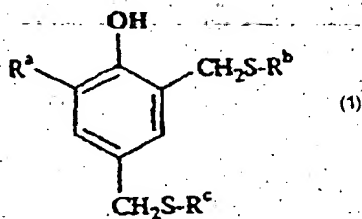
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(54) Title: LIQUID CURABLE RESIN COMPOSITION FOR OPTICAL FIBERS.



(57) Abstract: A liquid curable resin composition comprising for optical fibers (A) a urethane (meth)acrylate oligomer in particular an oligomer comprising a polyether backbone, (B) an unsaturated polymerizable compound, (C) a photoinitiator, and (D) an antioxidant which causes the cured coating to exhibit a yellowing index after five days exposure of less than 5, and a Youngs modulus retention rate of more than 70 % after aging for 30 days at 100 °C. In particular, component D can be a compound shown by the following formula (1), wherein R^a represents a hydrogen atom or an alkyl group having 1-4 carbon atoms and R^b and R^c individually represent alkyl groups having 1-12 carbon atoms, or 2-tert-butyl-6-(3'-tert-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate.

INTERNATIONAL SEARCH REPORT

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92 17535 A (RED SPOT PAINT & VARNISH CO. INC.) 15 October 1992 (1992-10-15)	
A	WO 99 31161 A (BORDEN CHEMICAL INC.) 24 June 1999 (1999-06-24)	
A	CHEMICAL ABSTRACTS, vol. 111, no. 10, 4 September 1989 (1989-09-04) Columbus, Ohio, US; abstract no. 82983, "RESIN COMPOSITIONS FOR OPTICAL FIBER COATINGS WITH LOW TRANSMISSION LOSS." page 316; XP000153090 abstract & JP 62 215663 A (SUMITOMO CHEM. CO. LTD.) 22 September 1987 (1987-09-22)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9217535	A	15-10-1992	AU 665948 B2	25-01-1996
			AU 1902292 A	02-11-1992
			BR 9205855 A	27-09-1994
			CA 2107353 A1	04-10-1992
			CZ 9302048 A3	16-03-1994
			DE 69229343 D1	08-07-1999
			DE 69229343 T2	03-02-2000
			DK 581872 T3	15-11-1999
			EP 0581872 A1	09-02-1994
			HK 1014193 A1	21-07-2000
			IE 921047 A1	07-10-1992
			JP 5098187 A	20-04-1993
			KR 243803 B1	01-02-2000
			MX 9201529 A1	01-10-1992
			WO 9217535 A1	15-10-1992
			US 6087413 A	11-07-2000
			US 5977200 A	02-11-1999
WO 9931161	A	24-06-1999	US 6048911 A	11-04-2000
			CN 1246874 T	08-03-2000
			EP 0964881 A1	22-12-1999
			NO 993874 A	27-09-1999
			WO 9931161 A1	24-06-1999
JP 62215663	A	22-09-1987	JP 7021124 B	08-03-1995

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